

PYROLYSIS OF METHANE AND THE C_2 HYDROCARBONS

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INTRODUCTION

Since its invention by Glick, Squire and Hertzberg (1), the single-pulse shock tube has been adopted by many investigators for chemical kinetic studies, so that it is rapidly developing into a standard laboratory tool. In this type of shock tube a sample of gas can be heated rapidly, held under known temperature and pressure conditions for a known time in the range of 0.1 to 10 milliseconds, cooled rapidly, and then removed for analysis. Optical and other measurements can be made on the gas during the heating time. In earlier shock tubes gas samples of known history could not be recovered. It is undoubtedly the ability to recover samples of reacted gas that has made this type of tube so popular with chemists, along with the fact that the shock tube is one of the few techniques for obtaining entirely homogeneous reaction data.

This paper is a review of recent shock-tube work as it applies to the pyrolysis of these simple hydrocarbons.

EXPERIMENTAL

Our shock tube is shown schematically in Fig. 1. It was made of 3-inch stainless steel pipe, the reaction section being 12 feet long and the driver section adjustable in length between 6 and 28 feet, so dwell times up to 15 milliseconds could be obtained with helium driver gas. The surge tank had a volume of about 50 cubic feet.

For measuring the incident shock speed, two SLM pressure transducers spaced 55 and 7 inches from the downstream end were used (a and b, Figure 1). The amplified signals from these were used to start and stop a microsecond timer, and also to start two oscilloscopes. One of these measured the pressure by means of a third SLM gauge, c, 3 inches from the downstream end, (see Figure 2) while the other measured the output from a photocell, d, mounted outside a window in the side of the shock tube, also 3 inches from the end (see Figure 3). Directly opposite the photocell window was a small tube leading to a quick-opening valve, e, from which samples of gas could be drawn for analysis.

Gas samples were analyzed before and after reaction by a vapor chromatograph. In spite of the fact that the driver gas was in direct contact with the sample during the experiments, no more than 5% driver

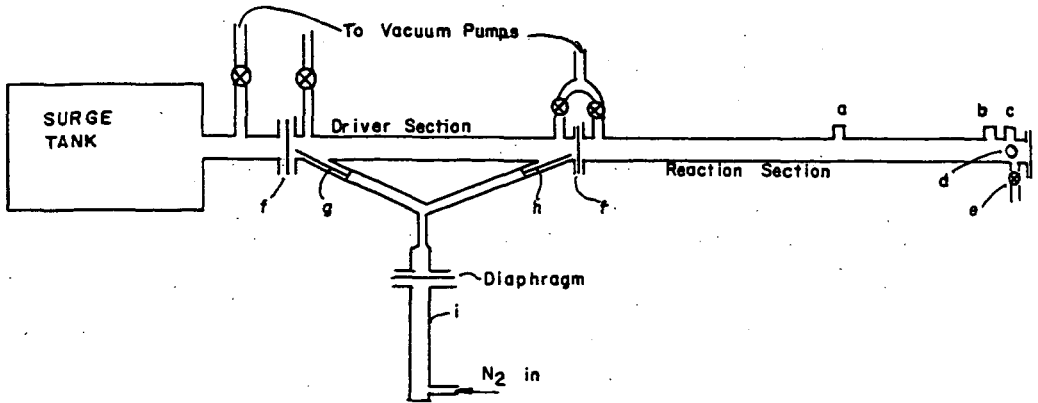


FIG. 1.
Schematic Drawing of Shock Tube

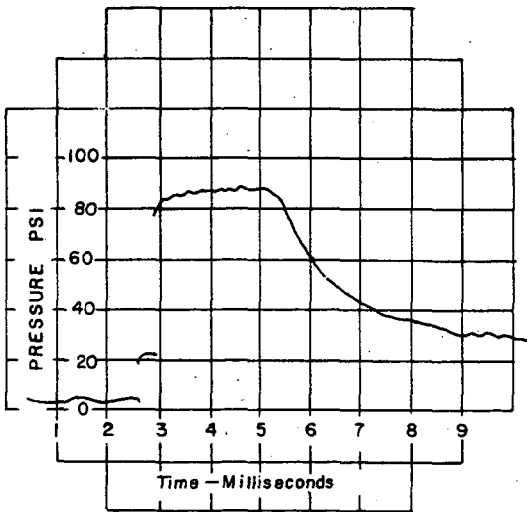


FIG. 2.
TYPICAL PRESSURE RECORD

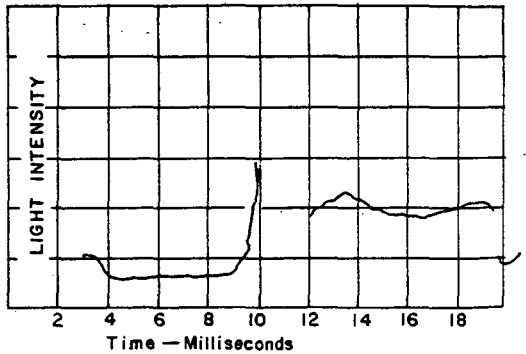


FIG. 3.
TYPICAL PHOTOMULTIPLIER RECORD

gas was found in the reactant gas after the runs, and in most cases the amount was less than 1%. As would be expected, the longer time runs showed the greatest contamination.

In a typical run, all sections of the shock tube were first evacuated, and then the sample and driver gases were added. Since the "tailored interface" technique (1) was used to give a pulse of uniform temperature, small amounts of nitrogen were usually added to the helium driver gas, to match it with the sample and pressure ratio. The two diaphragms *f* were then ruptured at the proper times, by the plungers *g* and *h* operated by the auxiliary shock tube 1, and a sample of gas taken for analysis a few seconds later. The oscilloscope traces were recorded with Polaroid cameras.

Strehlow and Cohen (2) have published a discussion of the reflected shock wave technique. They found that the most nearly ideal conditions for kinetic studies occurred when the sample gas was nearly all monatomic, while diatomic gases could be studied with some accuracy if measurements were taken near the end wall of the shock tube. With polyatomic gases, perturbations in the reflected shock wave due to boundary layer interactions were so great that temperatures could not be calculated with any accuracy. Polyatomic gases such as hydrocarbons must be highly diluted with a monatomic gas such as argon to give reasonably ideal conditions, and also to reduce the average specific heat of the sample gas to permit heating with reasonable driver/sample pressure ratios. It seems to have been satisfactorily demonstrated (3,4) that if these conditions are fulfilled, gas temperature calculated by the standard methods (5,6) are accurate to about 2%. However, we have found that in many runs the pressure, while coming to nearly the theoretical value just behind the shock wave, subsequently fluctuates for reasons we do not quite understand. We have corrected the calculated temperature by assuming that these fluctuations cause temperature changes according to the standard isentropic equations, and feel that these corrected temperatures are more accurate than uncorrected ones. Temperatures were also corrected for heat of chemical reaction.

RESULTS AND DISCUSSION

Methane. The rate of methane decomposition has been studied in three very similar single-pulse shock tubes by different investigators (7,8,9). There is agreement that the reaction is first-order in methane concentration, and that there is little inhibition of the reaction by products in the temperature range studied. The first-order rate constants are shown in Figure 6. On the whole, agreement among the three sets of data is reasonable, and though the activation energies calculated, 85 Kcal. (7), 93 Kcal. (9), and 101 Kcal. (8), differ, this may well be due to experimental error. None of these activation energies requires an unreasonable value of the frequency factor to give the observed rates. While the lower activation energies seem to fit in better with data obtained by other methods at lower temperatures (10,11), the possibility remains that some heterogeneous reaction occurred in the lower-temperature experiments, despite the investigators' best attempts to avoid it.

Figure 5 shows the product distribution in the pyrolysis of methane for heating times of 1.5 milliseconds at different temperatures, in terms of moles of each product formed per 100 moles CH_4 decomposing. Experiments at longer times show relatively more C_2H_2

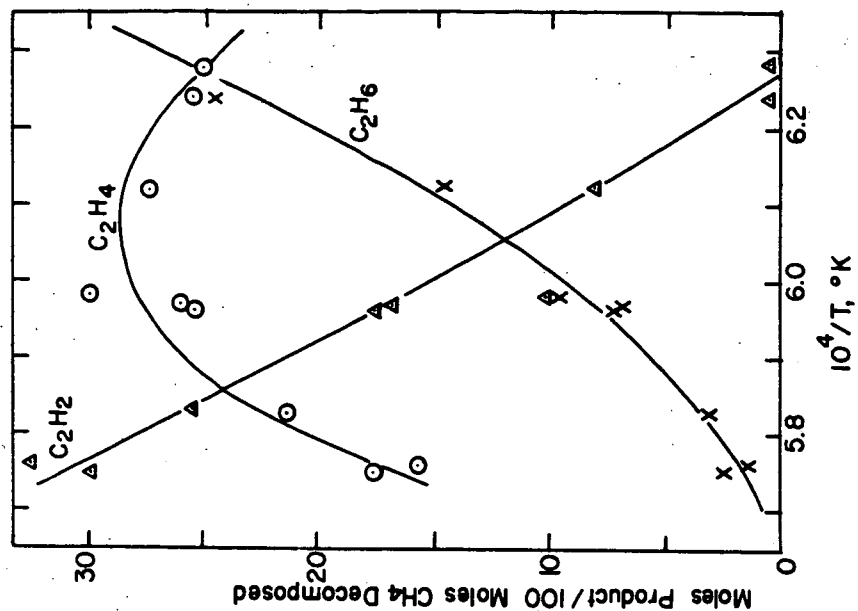


FIG. 5.
Product Distribution in Methane
Pyrolysis

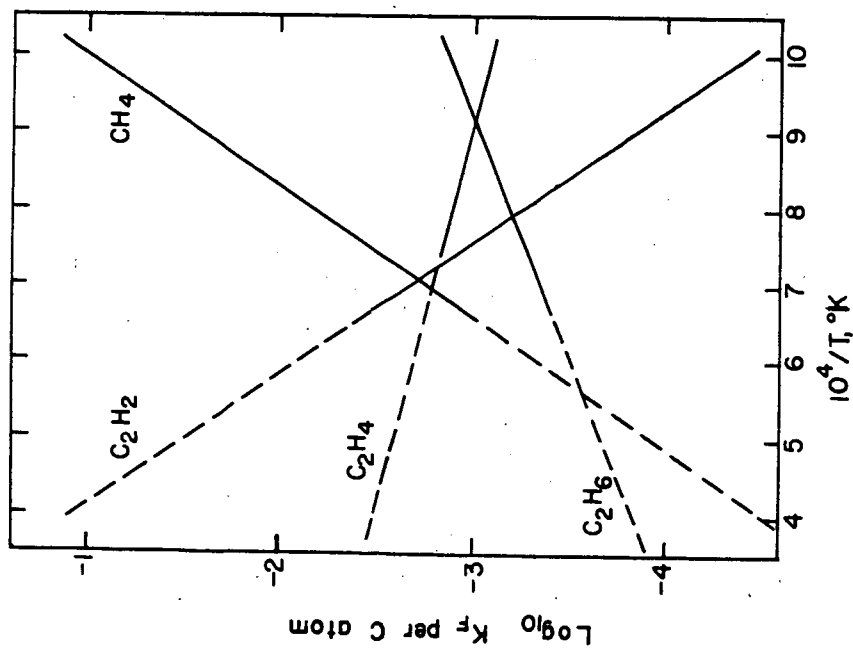
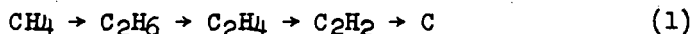


FIG. 4.
Equilibrium Data for CH_4 , C_2H_6 , C_2H_4 ,
and C_2H_2

and C_2H_4 , and less C_2H_6 , suggesting that C_2H_6 is an unstable intermediate. Methane pyrolysis thus seems to occur stepwise



although the C_2H_6 has a very short lifetime at high temperatures. There is a relation between the product yields of Figure 5 and the thermodynamic equilibrium data of Figure 4, which shows the relative stability of each molecule as a function of temperature, the species appearing highest on the graph being most stable. These data are taken from the NBS tables (12) although a very similar graph was made earlier by Kassel (13). The stepwise nature of the pyrolysis reaction is confirmed by comparison of these two Figures, since C_2H_6 and C_2H_4 show up more prominently in Figure 5 than would be expected from the equilibrium curves of Figure 4 alone.

The mechanism of conversion of CH_4 to C_2H_6 is still unsettled. Largely on the basis of our observed activation energy of 101 Kcal., we have preferred the series of reactions

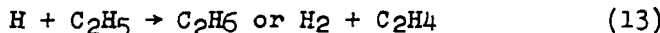
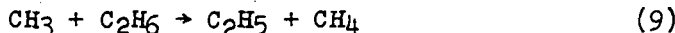


On the other hand, Kevorkian and co-workers (9) have preferred the reaction sequence



because it agrees better with their lower observed activation energy. These two reaction sequences both give first order kinetics with "chain length" of two, and it will require either some sort of direct observation on the reacting gas, or very accurate kinetic measurements, to decide between the two.

Ethane. Pyrolysis of ethane has for some time (14) been thought to occur by a free-radical chain mechanism, as follows:



A number of shock tube experiments (15) have given further verification of this reaction scheme. It has been found (as Steacie and Shane (16) for example found at lower temperatures) that one mole of

CH_4 is produced for each 20-25 moles of C_2H_6 in the first stages of pyrolysis. As pyrolysis proceeds, the rate constant falls off to less than a tenth of its original value, and the fraction of methane produced increases markedly. Ethane pyrolysis is strongly inhibited by methane, as would be expected from the above free radical steps and reaction 3. Inhibition by C_2H_4 also occurs. Quantitative calculations were made by using rate constants for the free radical reactions derived from various sources (and some estimates) which showed that these experimental observations should be expected from the above mechanism. Finally, with the assigned rate constants, the experimental results of several investigators could be reproduced over a wide range of temperatures, as shown in Figure 7.

From a series of experiments in a flow reactor in which ethane has been pyrolyzed in the presence of a small amount of radioactive methane, Brodskii and co-workers (17) have concluded that the above chain reaction is not the main one in the temperature range of 770-890°C. We are not altogether satisfied with their interpretation of their experimental data, and are making calculations to see if their observations can be interpreted in terms of the chain mechanism.

Ethylene. Shock tube studies on ethylene pyrolysis between 900 and 1600°C (18) show that there are two major reactions, one the formation of acetylene, which is a first-order reaction with an activation energy of 46 Kcal. over the upper part of the temperature range, the other the formation of 1,3-butadiene, which is second-order with an activation energy of about 25 Kcal. Butadiene formation is, of course, favored at low temperatures and high pressures, and acetylene at high temperatures and low pressures. Acetylene formation has been most thoroughly studied.

In contrast to ethane pyrolysis, this reaction does seem to be a molecular one in the classical sense, without the formation of free radicals. The most direct evidence for this is that the Arrhenius rate equation holds all the way from 2 to 95% ethylene decomposition, while for a chain reaction the rate should fall off at high conversions. Moreover, the product distribution (almost all hydrogen and acetylene at high temperatures and low pressures) remained the same up to 95% decomposition. The activation energy for acetylene formation is just slightly more than the heat of reaction (44 Kcal. at 1500°K.) (12), and we have not been able to think of a free-radical mechanism which would give this activation energy.

Experiments with an ethylene-acetylene mixture show that butadiene is not formed by reaction of ethylene with product acetylene, but comes more directly from ethylene, either by a straight bimolecular reaction, or perhaps through dimerization to butylene followed by loss of hydrogen. No butylenes were found, so they are unstable intermediates if they form at all.

Acetylene. Pyrolysis of acetylene has been studied in shock tubes by Greene, Taylor and Patterson (19) and by the author (20), between 900 and 2000°C. There is agreement that the overall reaction is second-order, and the observed rate constants are about the same. Acetylene is quite stable at high temperatures, compared to ethane and ethylene. The only difference in the two sets of data is that we found vinylacetylene and hydrogen to be the major pyrolysis products, while Greene found diacetylene to be a more important product than vinylacetylene. The latter compound seems without doubt to be the

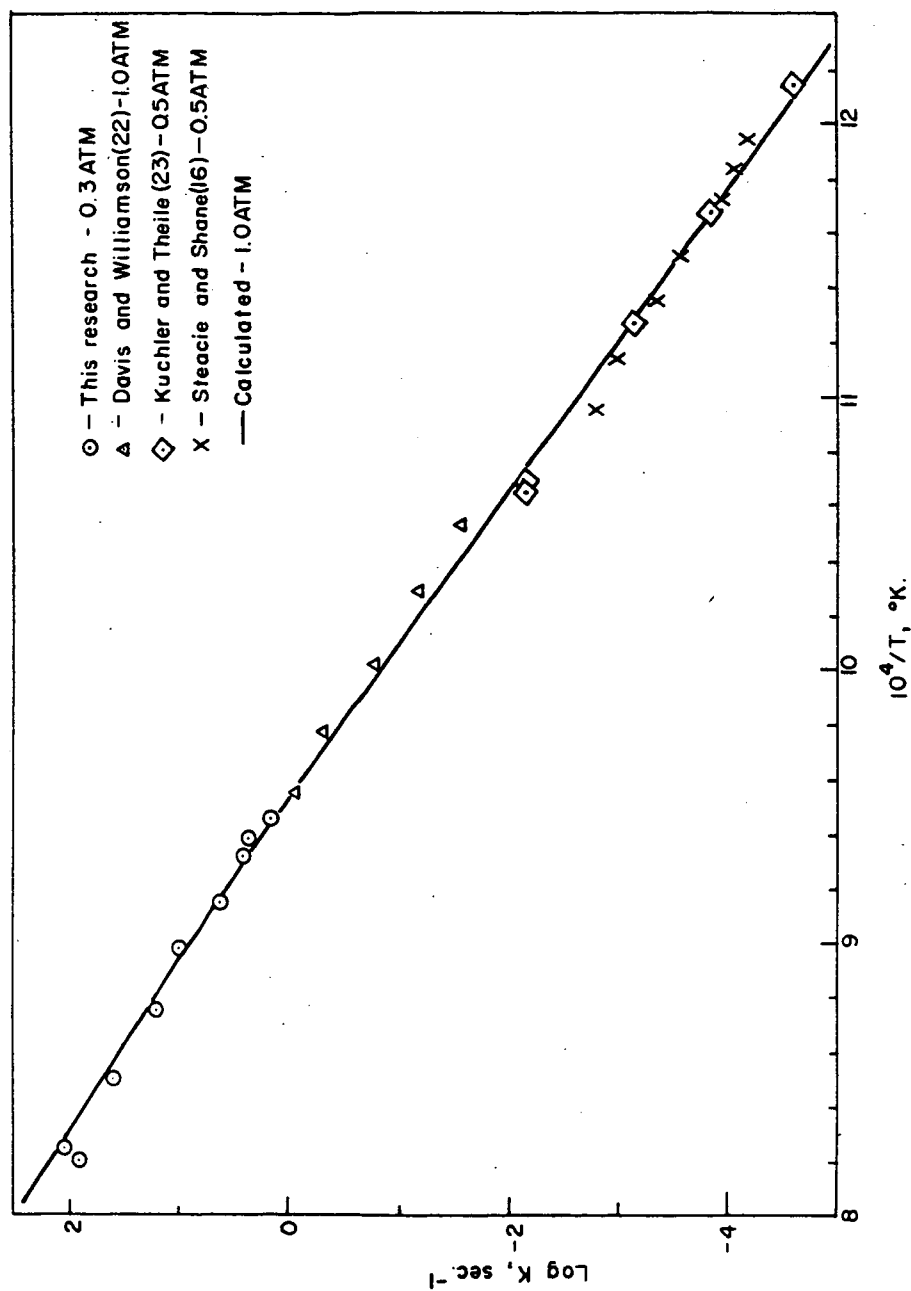


FIG. 7 Initial Rate Constants for Ethane Pyrolysis

first pyrolysis product of acetylene in this temperature range, since it appears at low conversions before any hydrogen is observed. The subsequent steps have not been defined, but probably involve further polymerizations and condensations to produce benzene and condensed aromatic compounds which eventually may be thought of as carbon, as discussed by Smith, Gordon and McNesby (21). These pyrolysis products intermediate between acetylene and carbon catalyze the decomposition reaction, so the rate increases as decomposition proceeds. When hydrogen was added to the acetylene, butadiene rather than vinylacetylene was formed, and the overall rate of acetylene decomposition was less than in the absence of hydrogen. That is, hydrogen inhibits acetylene decomposition by converting reactive vinylacetylene to relatively unreactive butadiene.

In conclusion, shock tube studies have added much to our understanding of the high temperature pyrolysis reactions of these simple hydrocarbons. On the other hand, many interesting problems remain to be solved.

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